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3,081,296

**ACYLATION OF STARCH AND CELLULOSE**  
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This invention relates to the preparation of cross-linked polysaccharide acylates. More particularly, it relates to the reaction of starch with a vinyl ester of a monocarboxylic acid whereby the starch is first acylated and then cross-linked with acetaldehyde.

This invention is a continuation-in-part of Serial No. 792,972 filed February 13, 1959, now Patent No. 3,022,289, which is a continuation-in-part of Serial No. 661,032, filed May 23, 1957, now abandoned, and Serial No. 673,172, filed July 22, 1957, now United States Patent 2,928,828. In Serial No. 792,972 we disclosed the acylation of starch with esters of a monocarboxylic acid and an ethylenically unsaturated alcohol. We have discovered that during this reaction an aldehyde, usually acetaldehyde, is generated in situ as a by-product. The aldehyde, which was generated in situ, was washed out as an unusable and deleterious by-product in all cases except where the acylating agent was a diester, namely allylidene diacetate. The allylidene diacetate produced acrolein in situ, which, having two functional etherifying groups, cross-linked the starch as the starch was acylated under alkaline conditions. While this reaction of allylidene diacetate has certain advantages the degree of cross-linking of the starch is not susceptible of control without the curtailment of the acylation function of the ester. In other words, the acylation and cross-linking reactions of allylidene diacetate are not independent since they occur at essentially the same pH.

The object of this invention is to prepare new cross-linked starch acylates from vinyl esters of a monocarboxylic acid, wherein the above described aldehyde by-product is utilized as an efficient cross-linking agent instead of being discarded.

Another object of this invention is to prepare cross-linked starch acylates from a single compound, which functions as both an acylating agent and a cross-linking agent, where the degree of cross-linking and extent of acylation can be controlled independently of each other.

Another object of this invention is to prepare granular cross-linked starch acylates having paste properties making them particularly suitable for use in making food products and in rock wool tile.

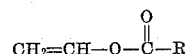
The objects of this invention are attained, generally speaking, by acylating starch with a vinyl ester of a monocarboxylic acid at an alkaline pH, whereby acetaldehyde is generated in situ, terminating said acylation reaction and initiating a cross-linking reaction with the generated acetaldehyde by adjusting the pH of the reaction to below 4. When the starch has been cross-linked to the desired degree, the cross-linking reaction is terminated by adjusting the pH of the reaction to about 5 or higher. In some cases the reaction may be allowed to continue until all of the generated aldehyde is used up.

The starch used in this invention may be any native starch, modified native starch or derivatized native starch having etherifiable hydroxyl groups. Corn starch, tapioca starch, wheat starch, rye starch, potato starch, sago starch, waxy corn starch and the amylose and amylopectin fractions therefrom are representative of the various native starches and starch fractions that may be used in this invention. Any of these starches may be modified by enzyme treatment, by oxidation with hypochlorite or by hydrolysis with an acid, for example, or derivatized by

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treatment with ethylene oxide, ethylene imine, etc. The starch derivatives also include other starch ethers, such as carboxyethyl or carboxymethyl starch, cross-linked starches, such as those disclosed in our Serial No. 102,365 filed on even date with this application, which are particularly suitable for pie fillings, etc. In those cases where derivatized starches are employed, the derivatized starch must have sufficient hydroxyl groups available for both the acylation and the cross-linking steps. In addition to the aforementioned starches, we can use various other polysaccharides, such as cellulose, carboxymethyl cellulose, methyl cellulose, cellulose acetate, inulin, etc.

The preferred vinyl esters are the vinyl esters of lower aliphatic acids, such as vinyl acetate, vinyl propionate and vinyl formate. The higher fatty acid esters of vinyl alcohol, such as vinyl butyrate, are not as reactive acylating agents as the lower fatty acid esters; however, useful results can be obtained even with vinyl stearate. Various other esters, such as vinyl chloroacetate, vinyl phenylacetate, vinyl benzoate, vinyl toluate, vinyl naphthenate, etc., can be used. All of the above compounds can be represented by the formula



wherein R is selected from the group consisting of alkyl having from 1-17 carbon atoms, haloalkyl having from 1-17 carbon atoms, aryl, alkaryl having from 1-23 carbon atoms and aralkyl having from 1-23 carbon atoms. These vinyl esters can be used in an amount equal to from about 0.5%-50% by weight of the dry starch in order to get products having from 0.1%-30% by weight monoacyl groups. In some cases the percent by weight of acyl groups in the starch acylate will be so low as to be within the experimental error of the determination for acyl groups. In those cases the presence of acyl groups in the product can be inferred from the change in the starch product (particularly the paste properties) which has been caused by the generated acetaldehyde. In all cases the degree of cross-linking of the starch by the generated acetaldehyde is independent of the amount of vinyl ester used since the cross-linking can be terminated at any point; a second cross-linking agent may be employed, if desired.

The preferred catalyst for the acylation reaction is one which buffers the reaction at about 9-10 pH. Sodium phosphate meets this requirement quite well. Other suitable catalysts are alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide; alkali metal salts, such as  $\text{Na}_2\text{CO}_3$  and mixtures of  $\text{NaCl}$  with  $\text{NaOH}$ ; ammonium hydroxide; quaternary ammonium hydroxides, such as tetramethyl ammonium hydroxide; amines, such as trimethyl amine and pyridine; etc. Useful reaction can be obtained over the pH range of about 7.5 to 12.5. Aqueous solutions of these alkaline catalysts can also be used to terminate the acetaldehyde cross-linking reaction.

The cross-linking catalysts, which also terminate the acylation reaction, are strong acids, such as sulfuric acid, hydrochloric acid and benzenesulfonic acid, which are capable of lowering the pH of the acylation medium to below 4.

In somewhat greater detail, granular starch is suspended in an aqueous medium in which the starch comprises about 2-70% by weight of the composition and then an alkaline catalyst is added to adjust the pH to the desired level between about 7.5 and 12.5. Alternatively, granular starch may be suspended in an aqueous alkaline medium. In either case, the starch may be pasted, if desired, prior to reaction with the vinyl ester or during either the acylation step or cross-linking step. In those cases where the starch is pasted, it can be used in that form, concentrated